Synthesis and Properties of Polymer Nanocomposites with Tunable Electromagnetic Response

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Synthesis and Properties of Polymer Nanocomposites with Tunable Electromagnetic Response

by

Kristen L. Stojak

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science Department of Physics College of Arts and Sciences University of South Florida

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Dedication

I would like to dedicate this thesis to my wonderful parents, Jane and David Devore, and my fiancé, Steven Repa. Without their love, support and encouragement, an endeavor such as this would have been near impossible. They are the foundation of who I am, who I have become, and who I am yet to be.

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Abstract

Multifunctional polymer nanocomposites (PNCs) are attractive for the design of tunable RF and microwave components such as flexible electronics, attenuators, and antennas due to cost-effectiveness and durability of polymeric matrices. In this work, three separate PNCs were synthesized. Magnetite (Fe$_3$O$_4$) and cobalt ferrite (CFO) nanoparticles, synthesized by thermal decomposition, were used as PNC fillers. Polymers used in this work were a commercial polymer provided by the Rogers Corporation (RP) and polyvinylidene fluoride (PVDF). PNCs in this thesis consist of Fe$_3$O$_4$ in RP, CFO in RP, and Fe$_3$O$_4$ in PVDF. Characterization techniques for determining morphology of the nanoparticles, and their resulting PNCs, include x-ray diffraction, transmission electron microscopy and magnetometry.

All magnetometry measurements were taken using a Quantum Design Physical Property Measurement System with a superconducting magnet. Temperature and external magnetic field magnetization measurements revealed that all samples exhibit superparamagnetic behavior at room temperature. Blocking temperature, coercivity and reduced remnant magnetization do not vary with concentration. Tunable saturation magnetization, based on nanoparticle loading, was observed across all PNCs, regardless of polymer or nanoparticle choice, indicating that this is an inherent property in all similar PNC materials.

Tunability studies of the magneto-dielectric PNCs were carried out by adding the PNC to cavity and microstrip linear resonator devices, and passing frequencies of 1-6 GHz through them in the presence of transverse external magnetic fields of up to 4.5 kOe, provided by an electromagnet. Microwave characteristics were extracted from scattering parameters of the PNCs. In all cases, losses were reduced, quality
factor was increased, and tunability of the resonance frequency was demonstrated. Strong magnetic field dependence was observed across all samples measured in this study.
Chapter 1: Introduction

1.1 General Introduction

The work completed in this thesis was motivated by the need to assist in ever changing and ever improving technologies related to miniaturization of high frequency devices. This thesis will discuss the creation and improvement upon past polymer nanocomposites (PNCs) [1, 2].

PNCs consist of two materials, a host polymer and some type of nano-sized filler. In the case of this thesis, the nano-sized fillers are comprised of magnetic nanoparticles, in particular, ferrites such as magnetite (Fe$_3$O$_4$) and cobalt ferrite (CoFe$_2$O$_4$). More about these ferrite nanoparticles will be discussed in subsequent chapters.

A polymer is chain of molecules, called monomers, which are covalently or ionically bonded to each other [3]. The polymer chains become cross-linked to each other through a process called curing. Oftentimes, the curing processes are irreversible because a chemical reaction takes place as a polymer cures. Polymers can become cured through a variety of physical and chemical methods. For example, photopolymers, like SU-8, become cross-linked when exposed to specific wavelengths of light. Thermosetting polymers (i.e. vulcanized rubber, Duroplast and many epoxies), or thermosets, become cured when exposed to a specific reaction temperature [3].

Types of polymers range from rubbers, resins, epoxies, plastics, and even phantoms, all of which can be employed for various applications. For example, polymethylmethacrylate (PMMA) is used in oncology as a phantom for radiology tests.
[4], but is also used as an ingredient in plexiglass. There are also conducting polymers, such as polyvinylidene fluoride (PVDF), which also acts as a piezoelectric. Piezoelectric materials produce an electric field when pressure is applied and also exhibit a stress change in the presence of an electric field [3]. Polystyrene is a common plastic used as an ingredient in plastic storage containers. And polyethylene glycol (PEG) is used as a biocompatible coating for nanoparticles, among other applications [5, 6].

1.2 Motivation Behind Research

Fabrication of lightweight, flexible and volume-efficient electrical components using PNCs is one of the major research focuses in the passive component sector for embedded technologies [7]. For instance, high dielectric constant PNCs are being studied to provide filtering, bypassing, and shielding for noise suppression in high-speed electronics. Extensive development and use of wireless communications have brought into focus the problem of electromagnetic interference (EMI) [8]. Shielding or absorbing of the electromagnetic field is considered an adequate solution for the EMI problem; however, the existing microwave absorbing materials have several drawbacks, such as being heavy, less durable and effective only over fixed frequency bands. Apart from shielding, PNCs are also very promising for microwave applications due to their potential for miniaturization, tunability and the realization of low-loss magneto-dielectric materials with similar permittivity and permeability values. Magneto-dielectrics have been shown to enable considerable improvements in the bandwidth and/or size reduction of microwave antennas [9, 10].

One of the promising ways to develop such materials is to exploit polymer composites reinforced with magnetic nanoparticles [2, 11]. However, the dispersion
of nanoparticles into a polymer matrix has been a challenging task for nanocomposite fabrication. Since the polymer matrix and inorganic nanoparticles often possess different polarities, a simple blending of particles and polymer will result in aggregation of particles [12]. One of the best ways to disperse nanoparticles uniformly in a polymer matrix is the surface functionalization of the particle with carefully selected organic surfactants. Different types of organic compounds are being used as surfactants to functionalize the nanoparticle surface, such as thiol, amine, carboxylic acids and so forth [13, 14]. If the particles are surface functionalized with organic surfactants, they will become more compatible and more homogeneously dispersed throughout the polymer matrix.

With specific regard to the EMI application, it has been observed that the high conductivity and dielectric constant of the PNC materials contribute to a high EMI shielding efficiency [15]. Recent reports on magnetic nanocomposites show improvements in EM wave absorption by using magnetic nanoparticles [16]. Since the metallic magnetic materials are conductive, the effective permeability decreases at high frequencies due to eddy current losses induced by electromagnetic waves [16]. However the eddy current loss can be suppressed if the particle size is below the skin depth. At the microwave frequencies of interest, the skin depth is around 1 μm [17] and therefore nanoparticles will be fully effective throughout their volume in EM wave absorption.

The objective of this work is to create a multifunctional PNC with magnetic nanoparticle fillers [12]. As part of this goal, the nanoparticles should be uniform in size and exhibit superparamagnetic properties. In past works on similar projects, agglomeration of nanoparticles has been a problem, as illustrated in the classic example shown in figure 1-1.
Agglomerations arise in PNCs because of the particle-particle interaction being stronger than the polymer-particle interaction [18]. It follows logically, that in order to have a functional PNC, free from agglomerations, the polymer-particle interactions must be dominant. This can be achieved by synthesizing nanoparticles with the appropriate surfactants prior to dispersion in the polymer. This thesis will demonstrate the possibility of creating new classes of PNCs that have tunable microwave and magnetic properties and, therefore, display multifunctionality.

1.3 Organization of Thesis

The present thesis aims to provide a systematic study of the synthesis and characterization of magnetically tunable polymer nanocomposites for advanced microwave device applications. Therefore, it is integrated into the following chapters:

Chapter 1 gives the overview and motivation of the MSc research work. The overall goals of the work are also presented.

Chapter 2 provides a general overview of magnetism, including the following magnetic states: diamagnetism, paramagnetism, ferromagnetism,
antiferromagnetism, ferrimagnetism, and superparamagnetism. This discussion will also include information on magnetic domains, finite size, and surface effects.

Chapter 3 presents and discusses the advantages and disadvantages of synthesis methods of ferrite nanoparticles and their polymer nanocomposites. Synthesis of nanoparticles is of utmost importance as different techniques can yield vastly different physical and chemical characteristics for the particles. Synthetic methods will also determine the yield of each batch of particles, which will, ultimately, be responsible for the amount of PNC and the quality of the end results. Chemical coprecipitation, microemulsion, solvothermal and thermal decomposition synthesis methods will be discussed. Methods for creating, coating and curing of the PNCs include a sol-gel drying technique, drop cast coating and spin-coating.

Chapter 4 describes the techniques used for structural and magnetic characterizations of the synthesized nanocomposites. Characterization techniques are integral to this work in that they determine the quality of the nanoparticles to be used in the PNCs and the PNCs themselves. Techniques that were used in this work include x-ray diffraction (XRD), transmission electron microscopy (TEM), and magnetometry. XRD was used to determine the phase of the various nanoparticles that were used for the PNCs and also to measure some of the PNCs. TEM was used to determine the size and shape of the nanoparticles for use in the PNCs and also to observe the uniformity of the PNC films. Magnetic measurements were carried out to observe the behavior of the magnetic nanoparticles alone and in the PNCs.

Chapter 5 covers the physical structure and properties of the ferrite nanoparticles used throughout this thesis. This is where the physical data will be presented about the nanoparticles and the PNCs. Data presented in this chapter will include XRD, TEM, and magnetometry data taken by a physical property measurement system (PPMS) with the alternating current measurement system (ACMS) option.
Chapter 6 presents and discusses the microwave properties of the synthesized nanocomposites. This chapter will focus on work completed by passing microwaves through PNCs under varying external magnetic field conditions in order to probe the multifunctionality of the samples. The data was taken using a performance network analyzer and an electromagnet with external magnetic field capabilities of up to ±5 kOe.

Chapter 7 summarizes the important results and achievements of the present thesis, as well as gives an outlook for future research directions in this exciting research field. This work will expand the current work to include one-dimensional nanostructures such as nanoparticle-filled carbon nanotubes, which may prove to be useful for enhancing inter-particle interactions and varying shape anisotropy within PNCs.
Chapter 2: Fundamental Aspects of Magnetism

Every material exhibits magnetism in one form or another because of magnetic moments that are inherent to all materials. Magnetic moments arise from unpaired electrons in atoms and their inherent spin. Since materials do not all have the same amount of unpaired electrons, they will display different types of magnetism, which is partially due to magnetic domains. These types of magnetism can partially be described by the magnetic susceptibility ($\chi = M/H$) [19]. Several different types of magnetism that will be discussed in this chapter are: (i) diamagnetism, (ii) paramagnetism, (iii) ferromagnetism, (iv) antiferromagnetism, (v) ferrimagnetism, and (vi) superparamagnetism.

It is worth noting that as material size is reduced below a critical size, the magnetic properties of the material are drastically altered from those seen in its bulk form. In particular, unlike their bulk ferro- or ferrimagnetic counterparts, nanoparticles that exhibit superparamagnetic properties are being widely used for a variety of applications ranging from magnetic recording to biomedical engineering [14]. As will be discussed in this thesis, such nanoparticles are ideally used for making tunable magneto-dielectric polymer nanocomposites for microwave applications.

2.1 Magnetic Domains

Magnetic domains are regions within a material that have uniform magnetization. The regions of uniform magnetization are due to preferred
directions, which arise from localized magnetic anisotropy throughout a crystal. Since these regions exist, different amounts of magnetic energy will be required to magnetize different samples. And various types of magnetism will be displayed in the different materials.

Between domains there exists a domain wall, where the gradual switching from a domain pointed in one direction to a domain pointed in the other direction takes place. It is possible for single domain (SD) regions to exist. Large particles energetically favor the formation of domain walls, resulting in multiple domains (MD). Magnetization reversal occurs via the nucleation and motion of these walls. As the particle size decreases toward a critical particle diameter \( D_c \) the formation of domain walls becomes energetically unfavorable and SD particles are consequently obtained [20-22]. In the case of larger particles, the magnetization process occurs mainly via a coherent rotation of magnetic moments, resulting in larger coercivity. As the particle size decreases to the SD region, the coercivity varies with the particle size. However, below superparamagnetic critical size \( D_{sp} \) the magnetic ordering state is easily collapsed due to thermal fluctuations, and superparamagnetism is exhibited. This will be covered in greater detail in section 2.7 of this chapter.

Furthermore, it has been shown that the critical grain size is dependent on the shape of the particle. For spherical particles with high anisotropy, the critical diameter \( D_c \) is determined by [21]

\[
D_c = \frac{9 \gamma}{2 \pi M_s^2} \simeq 1.44 \frac{\gamma}{M_s^2},
\]

where \( \gamma \simeq 4 \sqrt{AK} \) is the specific domain wall energy, \( A \) is the exchange constant, \( M_s \) is the saturation magnetization, and \( K_1 \) is the first-order anisotropy constant. It has been found that for cobalt ferrite (CoFe\(_2\)O\(_4\)) and magnetite (Fe\(_3\)O\(_4\)) spherical particles, the critical diameters are about 100 nm and 82 nm, respectively [23]. It is
worth noting that particles with significant shape anisotropy can remain single domain systems in much larger dimensions than their spherical counterparts.

### 2.2 Diamagnetism

Diamagnetism in a material arises when there are no unpaired electrons [24]. When this happens, the net magnetic moment of a material is zero, until forced into orientation by the application of an external magnetic field. The magnetic moments oppose the applied magnetic field, creating a very small, negative, unchanging susceptibility, as seen in figure 2-1. Examples of diamagnetic materials include copper, lead and mercury. Superconductors are also perfect diamagnets when they are in their superconducting state.

**Figure 2-1:** Cartoon showing what happens in a diamagnetic material before, during, and after it is brought into contact with an external magnetic field.

### 2.3 Paramagnetism

Paramagnetism in materials arises when unpaired electrons do exist in that material [24]. The magnetic moments in a paramagnetic material are initially randomized, but will tend toward the direction of an external magnetic field, as seen in figure 2-2.
Figure 2-2: Cartoon showing what happens in a paramagnetic material before, during, and after it is brought into contact with an external magnetic field.

Where paramagnetism differs from diamagnetism is that the susceptibility created by this class of materials is positive and unchanging. Hence, the magnetic moments that align in the same direction as the magnetic field are weakly interacting. This also implies that when the external magnetic field is removed, the magnetization returns to zero. Paramagnetic and diamagnetic materials are often considered non-magnetic. Examples of paramagnetic materials are aluminum, magnesium, and tungsten.

2.4 Ferromagnetism

Ferromagnetism in materials arises when unpaired electrons exist and strong interactions between magnetic moments are present [24], as figure 2-3 shows. These strong interactions occur below a characteristic temperature (Curie temperature), at which a phase transition takes place from a paramagnetic to a ferromagnetic state.
Unlike with paramagnetism, the susceptibility of the sample is not constant with external magnetic field. An example of a plot of magnetization as a function of applied magnetic field can be seen in figure 2-4.

From this plot, features are observed that are not seen in the previous two discussed magnetic states. One such feature is saturation magnetization \(M_S\). \(M_S\) occurs when the magnetic moments are completely aligned with the external magnetic field. \(M_R\) is the remnant magnetization after the fully magnetized sample is demagnetized (i.e. the external magnetic field is brought to zero). \(M_R\) is observed after a sample has been saturated in either the positive or negative direction. The coercivity \(H_C\) is where the magnetization of the sample finally reaches zero after saturation.
Therefore, $H_C$ is the magnetic field needed to switch the alignment of magnetic moments from one direction to another. It should be noted that depending upon the magnitude of $H_C$, ferromagnets can be categorized into soft ($H_C$=small) and hard ($H_C$=large) materials. Some examples of ferromagnetic materials are cobalt, iron and gadolinium.

### 2.5 Antiferromagnetism

Antiferromagnetism arises when the nearest neighbor magnetic moments in a material point in opposite directions [24]. This pattern of magnetic moments arises from two separate sublattices of magnetic moments that are separately ordered ferromagnetically, but in opposite directions.

![Figure 2-5: Cartoon showing what happens in an antiferromagnetic material before it is brought into contact with an external magnetic field and when it encounters small and big external magnetic fields.](image)

As figure 2-5 shows, in the absence of an external magnetic field, antiferromagnetic materials have no net magnetization. Analogous to the Curie temperature of ferromagnets, there exists a transition temperature with antiferromagnets called the Néel Temperature, above which the sample displays paramagnetism. If an external magnetic field is strong enough, the magnetic moments in the oppositely oriented sublattice will conform to the first one, and all magnetic moments in the material will
be aligned, thus saturating the sample. Some examples include hematite (\(\alpha-\text{Fe}_2\text{O}_3\)), chromium and, nickel oxide (NiO).

2.6 Ferrimagnetism

Ferrimagnetism shares some similarities with ferromagnetism and antiferromagnetism [24]. Like with antiferromagnetism, ferrimagnetism arises from the formation of two oppositely aligned magnetic sublattices. However the sublattices have different magnitudes for their magnetic moments leading to an overall magnetization in one direction, much like ferromagnetism, as illustrated in figure 2-6.

*Figure 2-6:* Cartoon showing what happens in a ferrimagnetic material before, during, and after it is brought into contact with an external magnetic field.

Because of this, the sample appears to behave much like a ferromagnet. Many materials that display ferrimagnetism have spinel or inverse spinel crystalline structures, meaning that they are of the form \(AB_2\text{O}_4\), which will be further discussed in subsequent chapters. Materials discussed in this thesis are of the inverse spinel structure, such as cobalt ferrite (CoFe\(_2\)O\(_4\)) and magnetite (Fe\(_3\)O\(_4\), Fe\(^{2+}\)Fe\(^{3+}\)\(_2\)O\(^{2-}\)).
2.7 Superparamagnetism/Single Domain

As previously eluded to, superparamagnetism is a size and temperature dependent magnetic property in materials. When particle size is reduced to a critical size, the formation of domain walls becomes energetically unfavorable and the single domain (SD) regime is achieved.

When in the SD regime, at lower temperatures, anisotropy energy, $KV$, dominates the behavior of the sample and thermal fluctuations are suppressed \([14, 24]\). This would happen below the blocking temperature ($T_B$), where nanoparticles are in the ferro- or ferrimagnetic state. Here, the nanoparticles are in the the ferro- or ferrimagnetic state. At higher temperatures, thermal energy, $k_BT$, dominates the samples and they are thermally fluctuating. When an external magnetic field is applied, magnetic energy dominates over the thermal fluctuations and magnetic moments align, as shown in figure 2-7.

![Figure 2-7](image.png)

**Figure 2-7:** Cartoon showing what happens in a superparamagnetic material before, during, and after it is brought into contact with an external magnetic field.

Between thermal fluctuations and surface spin disorder, which will be discussed briefly later in this chapter, nanoparticles in the superparamagnetic regime will never quite reach saturation, but will come very close to it.

As previously mentioned, superparamagnetism arises in ferro- or ferrimagnetic materials due to reduction in size. Refinement of particle size in magnetic materials is essential for obtaining desired magnetic properties. It has been
shown that reducing ferro- or ferrimagnetic particles down to below 100 nm can lead to an appearance of anomalous magnetic properties [20, 21]. As a ferro- or ferrimagnetic particle reaches a critical grain size, \( D_C \), it becomes a SD particle [21]. As particle size decreases below \( D_C \), the magnetic properties of the material are significantly affected. The dependence of \( H_C \) on the particle size of a magnetic material is illustrated in figure 2-8. It is important to note herein that in the superparamagnetic state, the material exhibits zero coercivity (no magnetic losses) and its magnetization reaches saturation in a very small applied magnetic field (a few hundreds of Oe). This distinguishes a superparamagnetic material from a ferromagnet or a paramagnet. Provided that the ferrite nanoparticles studied in the present thesis are superparamagnetic at room temperature, they are ideal for being incorporated into a polymer matrix to make tunable magneto-dielectric nanocomposites for microwave applications.

![Graph showing the dependence of coercivity on particle size.](image)

**Figure 2-8:** Particle size (D) dependence of coercivity (\( H_C \)): \( H_C \sim 0 \) as \( D < D_{sp} \); \( H_C \sim D^6 \) as \( D_{sp} < D < D_C \); \( H_C \sim D^n \) as \( D > D_C \). \( D_{sp} \) and \( D_C \) are the superparamagnetism and critical size thresholds. SPM, SD, and MD stand for superparamagnetic, single-domain, and multiple domain structures, respectively [16].

It is also worth noting that, in fine particle systems, when a large enough fraction of atoms resides at the surface of a particle, the broken exchange bonds are sufficient to induce surface spin disorder thus creating a core-shell structure made of
the ferrite core with a shell of disordered spins [25, 26]. The fraction of spins on the surface of nanoparticles increases with decrease in particle size. By assuming a core-shell structure with a magnetically dead shell of thickness $d$, that does not contribute to the saturation magnetization $M_s$, the variation of $M_s$ with particle size $D$ can be expressed by [27]

$$M_s = M_0 \left(1 - 2d/D\right)^3,$$  

where $M_0$ is the saturation magnetization of the bulk form of the same material.

The high surface-to-volume ratio of 4 nm nanoparticles results in a shell of disordered surface spins that has also been shown to be responsible for inducing exchange bias (EB) [27]. The energy required to rotate spins in exchange biased materials contributes to enhanced coercivity below the spin freezing temperature as well as open, irreversible hysteresis up to high fields [25, 26, 28-30].
Chapter 3: Synthesis of Ferrite Nanoparticles and Their Polymer Nanocomposites

3.1 Nanoparticle Synthesis Methods

The synthetic method for making ferrite nanoparticles can drastically change their physical properties, such as size, shape, and displayed magnetic properties. The synthetic technique used to make ferrite nanoparticles also determines how the surface is coated to allow for suspension in different types of solvents such as hexane or water.

There are a wide variety of synthetic techniques available for making ferrite nanoparticles and polymer nanocomposites (PNCs). For nanoparticle synthesis, common techniques are bottom-up approaches, meaning that nanoparticles are built up from agglomerations of atoms. This chapter will discuss four common synthetic techniques for making nanoparticles: (i) co-precipitation, (ii) microemulsion, (iii) solvothermal and (iv) thermal decomposition. Also discussed is the creation of PNCs, which includes techniques such as: (i) sol-gel drying, (ii) spin-coating, and (iii) drop-cast. Curing methods for the PNCs will be covered as well. Thermal decomposition was exclusively used for the nanoparticle synthesis and a drop-cast method was used for PNC creation and device filling. These points will be further elaborated upon later in this chapter.
3.1.1 Chemical Co-Precipitation

*Chemical co-precipitation* is the most commonly used synthetic technique for making ferrite materials due to ease and relative cost effectiveness of this method. The first step is to make a starting solution containing desired chemical substances. When a specific material is added to this solution, an instant reaction occurs. As the name implies, the reaction splits the solution into a supernatant and a precipitate. The precipitate consists of nanoparticles.

This is a quick method that can be used to make several different types of materials with excellent phase and shape uniformity, but is often associated with a large size distribution [31-33]. For example, the method for making magnetite (Fe$_3$O$_4$) nanoparticles involves combining ferrous (Fe$^{2+}$) and ferric (Fe$^{3+}$) salts with an acidic material and precipitating the desired particles with a very alkaline substance [32]. The ferrous and ferric salts are generally iron chlorides, sulfates or nitrates. Hydrochloric acid is one example of an acid used for this procedure [31]. Water is also commonly used as the carrier solvent for the salts during this reaction. Ammonia and sodium hydroxide are frequently used as the base because of their strong alkaline nature. The reaction can be allowed to take place at room temperature or an elevated temperature. If the reaction takes place at elevated temperature, it is crucial to have an inert atmosphere to avoid undesired phases of ferrite materials.

Once all of the precipitate has formed, the reaction is finished and it is vital to wash the nanoparticles by centrifugation in the presence of ethanol and water to remove any unreacted chemicals from the final product. Figure 3-1 shows a cartoon of the chemical co-precipitation synthetic route.
If surface functionalization is required, surfactants are often added after the chemical co-precipitation is finished. This must be done carefully because ferrite nanoparticles can easily be oxidized. For example, magnetite nanoparticles can be easily oxidized to maghemite ($\gamma$-Fe$_2$O$_3$) when exposed to ambient conditions. It is possible to add a polymer during or just after the reaction to surface functionalize the nanoparticles, thus protecting them from further oxidation. It has been reported that surfactants in aqueous solutions, such as sodium oleic acid, dodecylamine, and sodium carboxymethyl cellulose can be added during the chemical co-precipitation procedure. It is possible to add a polymer in lieu of a surfactant. This could be done during the reaction by having water as the initial carrier solvent along with a polymer, such as polyvinyl alcohol (PVA) [33]. The rest of the reaction would then carry on as before and the phase of the nanoparticles would remain intact.

### 3.1.2 Microemulsion

The synthesis of nanoparticles by *microemulsion* has an advantage of the excellent control over shape, size, and phase of resulting particles, together with relative ease [31, 34]. The drawback is that there is a very small yield of resulting nanoparticles.
Microemulsion involves the mixing of two immiscible liquids in the presence of metal salts to create the desired material. There are two types of microemulsion synthetic process possible, water-in-oil and oil-in-water microemulsions [31]. When the two immiscible liquids are mixed together, one forms microdroplets in the other. These microdroplets are stabilized in the solution by surfactants; hence the surfactant plays a crucial role in this synthetic technique, acting as a stabilizing agent for the entire solution rather than just the resulting nanoparticles. The surfactant film is the boundary between the microdroplets and the encompassing solution [34]. In case of an oil-in-water microemulsion, the microdroplets are called micelles, with the hydrophilic head of the surfactant facing out, towards the water. In case of a water-in-oil microemulsion, the microdroplets are appropriately called reverse micelles because the hydrophilic head of the surfactant faces the center. The size of the micelles or reverse micelles is determined by the water-to-oil ratio within the vessel.

To create ferrite nanoparticles, two separate water-in-oil microemulsions are required [31, 34]. The reverse micelles contain the necessary reactants to form the desired nanoparticles. The two microemulsions are then mixed together with collisions between the two types of reverse micelle occurring. The droplets are dominated by Brownian motion because of their small size and rarely remain stuck together. This collision and separation process creates nucleation and growth of nanoparticles in the form of a precipitate within the reverse micelles. The precipitate contains the desired nanoparticles as shown in Fig. 3-2 (A).
As detailed in Fig. 3.2 (B), the two microemulsions are sonicated after combination to create one coherent microemulsion, which is then vigorously stirred until a transparent solution is obtained. The solution is stirred for several hours at room temperature until the initial reaction stabilizes. At this point, slow heating under an inert gas takes place until the precipitate is formed, and the solution is left...
to reflux at full temperature until the reaction ends. Finally the reacted solution is centrifuged to remove any undesired chemicals and the resulting nanoparticles can be suspended in an organic solvent.

### 3.1.3 Solvothermal

The *solvothermal* synthetic route consists of placing a mixture of metallic precursor solutions with surfactants and solvent into a sealed autoclave to create nanoparticles by applying pressure [31, 35]. When the solvent is water, this method is called *hydrothermal* synthesis. After the materials are added to the sealed autoclave, the entire setup is placed into a constant temperature vessel, such as a water, oil, or sand bath and heated to an elevated temperature to “pressure cook” the materials. The resulting material produces a small yield; however the particles formed are typically very uniform in size and shape [31]. Figure 3-3 shows a diagram of the solvothermal synthetic technique.

**Figure 3-3:** Autoclave to be suspended in a constant temperature water, oil, or sand bath, depending on the temperature requirements of the reaction. This schematic shows the mixed metallic precursor solutions and the pressurized vapors they create, with nanoparticles beginning to form in solution [14].

### 3.1.4 Thermal Decomposition

*Thermal decomposition* is a very common synthetic technique for making ferrite nanoparticles due to the quality of the resulting nanoparticles and the speed
of the reaction [5, 31, 36-42]. As the name *thermal decomposition* implies, this technique takes advantage of materials breaking down and forming new compositions at various temperatures. This technique is particularly useful for making very small, uniform nanocrystals. The basic procedure [31] is to mix organometallic compounds with a surfactant to stabilize the particles in a high boiling point organic solvent. The organometallic materials are generally metal acetylacetonates \([\text{M(acac)}_n, \text{M} = \text{Fe, Mn, Co, Ni, Cr}, n = 2, 3]\), metal cupferronates \([\text{M}_x\text{Cup}_x, \text{M} = \text{metal ion}, \text{Cup} = \text{N-nitrosophenylhydroxylamine}]\), or carbonyls. The surfactant, or surface active agent, is used as a stabilizing coating for the nanoparticles. The surfactant determines what types of solvent the synthesized nanoparticles can be dispersed in, and prevents them from further oxidation. Fatty acids such as oleic acid, hexadecylamine and oleylamine are common surfactants for this technique [36]. Benzyl ether, phenyl ether, octyl ether, or 1-octadecene can be used as the high boiling point organic solvents. Generally there is also use of an alcohol as a cosurfactant. Some commonly used alcohols are 1,2-hexadecanediol, 1,2-tetradecanediol, or 1,2-dodecanediol. Figure 3-4 shows how the various reagents come together to create a ferrite nanoparticle.

![Figure 3-4](image_url)

**Figure 3-4:** This flow chart shows how to synthesize inverse spinel nanoparticles using thermal decomposition with an oleate coating. The reagents are as follows: \(\text{Fe(acac)}_3\), iron (III) acetylacetonate, as an organometallic material; \(\text{ROH}\), a hydroxyl, with 1,2-hexadecanediol as an example; \(\text{RCOOH}\) as a carboxyl, with oleic acid as an example; \(\text{RNH}_2\) as an amine, with oleylamine as an example; and a solvent. The phase of the resulting nanoparticles would be \(\text{MFe}_2\text{O}_4\) with “M” standing for transition metal [13, 14].

The nanoparticles discussed in subsequent chapters were produced via thermal decomposition. To create the ferrite nanoparticles, first, all reagents are mixed together in one flask; this includes all organometallic materials, surfactants,
alcohols, and solvents. After mixing, oxygen is purged from the flask using argon, and heating is commenced. The flask is heated to the first reaction temperature, where the precursor will decompose. After two hours, the vessel is heated to the reflux temperature and the nanoparticles are formed. After one hour, the reaction is terminated by removing the heat source, rapidly cooling the reaction vessel. One of the advantages of thermal decomposition is that it is a \textit{one-pot synthesis} meaning that multiple chemical reactions occur in one reaction flask. Once the particles are formed, the sample is centrifuged several times in the presence of ethanol to wash the nanoparticles and remove any excess chemical waste. After ethanol centrifugation, the nanoparticles are centrifuged in the presence of hexane. Any particles that are not able to stay in suspension are discarded because they are either too large, or have an insufficient surfactant coating. The final product of ferrite nanoparticles, such as magnetite or cobalt ferrite, in a non-polar solvent is a ferrofluid. Most often, nanoparticles were suspended in hexane.

\textbf{3.2 PNC Synthesis and Device Coating}

Once the nanoparticles are synthesized, the polymer nanocomposite (PNC) can be created. There are multiple methods that can be employed to make a PNC. This work primarily utilized a solution mixing method that was optimized for \textit{Rogers Polymer} (RP) and \textit{polyvinylidene fluoride} (PVDF) as well as the surface functionalization of the synthesized nanoparticles.

\textbf{3.2.1 Weight Percentage}

All PNCs in this work were measured by weight percentages. This means that the concentration of the nanoparticles in the polymer was determined by calculating weight percentage of the nanoparticles. The main polymer used in this work, RP,
which is a high-temperature thermosetting resin housed in a xylene solution. The first step in the PNC synthesis is to determine the percent solids of the RP-xylene solution. This was done by dropping a known amount of polymer solution into two weighing trays and measuring the mass before and after the xylene and other solvents evaporated. By taking this ratio of masses, the percent solids of the polymer solution can be found. The desired amount of dry polymer can be found using the following equation:

\[
\frac{y}{\% \text{solids}} = z, \tag{3.1}
\]

where \( y \) is the dry mass of the polymer, \( \% \text{solids} \) is the percentage of dry polymer in the RP solution, and \( z \) is the mass of the polymer solution. Once calculated, the nanoparticles were dried and measured out to the specific weight percentages using the following equation:

\[
\frac{\text{wt}\%}{100}(x + y) = x, \tag{3.2}
\]

where \( \text{wt}\% \) is the weight percentage of dry nanoparticles in the polymer, \( x \) is the mass of the particles and \( y \) is the dry mass of the polymer. The weighted nanoparticles were placed in a vial and the calculated amount of polymer was added to the vial. If any discrepancy of polymer solution weight was present, the new weight percentage was recorded. Once the polymer and nanoparticles were combined, hexane was added and the solution was stirred overnight with a magnetic stir bar to ensure even mixing within the PNC.

When using PVDF, a powder form of the polymer was used, making the determination of weight percentages much more straightforward. As with the solution method, the dry particles were measured out in a vial and then the dry PVDF powder was added to the vial as well. After the polymer and nanoparticles were combined, water was added to create a PNC solution, for easier coating of structures.
The PNC solution was then stirred overnight to ensure even dispersion of nanoparticles within the polymer.

### 3.2.2: Sol Gel Drying Method

Once the PNCs are created, there are various ways to coat different devices and evaporate the solvent. One drying method for the polymer is similar to a sol-gel nanoparticle synthesis method [43]. A PNC solution is made, as previously described, and then the solvent is slowly evaporated from the PNC until a rubbery PNC remains. This is generally done in a rotational evaporator (roto-vap) as seen in figure 3-5.

![Figure 3-5: This image shows an example of a rotational evaporator that can be used to dry out PNCs and other materials.](image)

This roto-vap contains a vessel seated at an angle that holds the PNC solution sitting in a boiling water bath. As the solution heats, the solvent evaporates into another portion of the roto-vap set-up and is condensed into a solvent trap by using cold water, dry ice, etc. This drying method differs from a typical sol-gel method in the sense that all solvent is evaporated from the vessel, leaving a dry PNC, which can be rubbery. The problem with this PNC drying method is that it can be challenging to
mold the dry, rubber-like PNC into a device, particularly a small one, as the material is not conducive to hand-powered compression.

### 3.2.3 Spin-Coating Method

The spin-coating method is utilized often when a thin layer of material is needed over a relatively small surface area. The substrate to be coated is placed on a vacuum-sealed substrate holder and rotated at specific revolutions per minute (RPM). Once the substrate is in motion, a PNC solution is dropped directly on to the substrate and it immediately spreads out, covering the substrate [2]. The thickness of the film is determined by the viscosity of the PNC solution, the RPM of the spin-coater, and how many layers of material are added. Since a thinner film can be made, evaporation of the solvent can happen more quickly than with a drop-cast method and the films can be thinner. One challenge with the spin-coating method is that the film usually has a bead at the edge, where material gathers while rotating and this can interfere with any microwave or RF measurements. The other large challenge is that any size or depth cavity/substrate cannot be filled. For this reason the spin coating method was used in previous works on PNCs, but was not employed in the scope of this thesis.

### 3.2.4 Drop-Cast Method

The method that was most often employed in this thesis is the drop-cast method [18]. Because of the varying shapes and sizes of devices to be coated for this work, the most effective method for coating them and filling cavities was by dropping the solution into the desired volume. For this method, a reasonable amount of solvent should be present in the PNC. It should be relatively easy to draw the PNC into a syringe to drop a pre-determined amount of PNC on to the device. Once the material is dropped on to the device, the solvent is either left to dry on its own or subjected to mild heating in a vacuum oven, to ensure that no changes in
morphology, such as size, shape or phase, of the nanoparticles would occur. The main challenge with this method is that it takes a bit more patience, as it takes longer for the solvent to evaporate on its own. However, the main benefits are that it is easier to achieve thicker, more uniform films and almost any size or shape cavity can be filled.

### 3.3 PNC Curing

After the PNCs have been created and the devices have been coated, it is crucial to cure the PNC. As previously mentioned, *curing* refers to the process by which the polymer chains are cross-linked to each other [3]. This irreversible physical and chemical changes solidifies and strengthens the polymer. There are multiple methods by which curing can take place such as curing by hot press and by vacuum oven.

#### 3.3.1 Curing by Hot Press

Depending on the polymer, a hot-press can be used to cure the PNC. For our purposes, with a high-temperature thermosetting resin, like RP, a hot-press is an appropriate way to cure large amounts of the material. For this method, a dry PNC, in its rubbery form, would be placed in some sort of mask, and then placed in a press that is capable of heating to temperatures around 300°F and pressing to pressures on the order of 10,000 psi. After one hour of being heated and pressed, the mask, containing the PNC, is cooled down and the hardened PNC is removed from the mask.
Figure 3-6: This figure shows PNCs that were cured using the hot press method and have come out of a short, cylindrical mask.

This method is best for large amounts of material or very thick layers, for example, the PNCs in figure 3-6 are 1-2 inches in diameter. A risk that is presented when curing a PNC with this method is that the particles can be subjected to a morphology change upon extreme heating and/or pressure. Only robust particles should be used when employing hot presses to cure the PNCs. This curing method would not be suitable for curing PNCs that are part of delicate devices.

3.3.2 Vacuum Oven Curing

A more gentle way to cure thermosetting polymers is to heat them with the lack of pressure. Once the PNC is in place on a device, the solvent is left to evaporate on its own or heated slightly. Once the dry PNC sits in the device, it is placed in a vacuum oven and heated gently, in our case 80°C, to ensure no morphology change [11, 18, 44]. Once again, patience is needed with this method, as it can take up to 24 hours for the PNC to cure with the lack of pressure. The length of curing time is dependent on nanoparticle content and PNC thickness in the device. This method was exclusively employed in the scope of this thesis.
Chapter 4: Characterization Techniques

4.1 X-Ray Diffraction (XRD)

4.1.1 Basic Principles of XRD

X-ray diffraction (XRD) serves as a relatively cheap, easy and accurate way to characterize samples, therefore it has become a standard way of doing so. XRD is based on the diffraction of x-rays off of a crystalline lattice. Each material has a specific “fingerprint” that can be read with the use of XRD.

\[ n\lambda = 2d\sin\theta \]  

\[ (4.1) \]

**Figure 4-1:** Schematic showing Bragg diffraction for x-ray diffraction (XRD) [45].

As figure 4-1 shows, x-rays incident on the sample collide with atoms in a lattice structure and are diffracted back and gathered by a detector. Interference of x-rays, which arises from path length differences, are described by the Bragg equation [46]:

\[ n\lambda = 2d\sin\theta \]  

\[ (4.1) \]
where \( d \) is the spacing between the crystalline lattice plains, \( \lambda \) is the wavelength of the x-rays, \( n \) is an integer and \( \theta \) is the angle of incidence between the incoming x-rays and the surface of the sample. The diffracted x-rays interfere with one another to create diffraction patterns, creating a series of peaks of various heights in different locations corresponding to the crystallinity of the sample. For example, cobalt ferrite is an inverse spinel material, as shown in figure 4-2.

\[ \text{Spinel and inverse spinel structures have the molecular formula } AB_2O_4, \text{ where } A \text{ and } B \text{ are transition metals and } O \text{ is oxygen. In the case of cobalt ferrite, } A^{2+} \text{ would be cobalt and } B^{3+} \text{ would be iron.} \]

\[ \text{Figure 4-2: Inverse spinel crystalline structure for cobalt ferrite [47].} \]

\[ \text{Figure 4-3: Shows an XRD pattern of cobalt ferrite nanoparticles. The numbers located at each peak are Miller indices.} \]
An XRD pattern is seen in figure 4-3; this pattern is for cobalt ferrite nanoparticles. The numbers at the top of each peak are Miller indices describing where atoms are within each unit cell of the crystalline lattice.

### 4.1.2 Sample Preparation for XRD

XRD samples can be made a variety of ways, depending on the sample and the particular x-ray diffractometer. Many thin films can be measured as they come, as long as they fit within the incident beam’s range. However, loose, surfactant-free powders generally need to be pressed into a mold before being measured, as to ensure that the material will create a uniform layer and will not spill off of a substrate during measurement. If a powder has a surfactant in it, like the ones described in this thesis, it is possible that the surfactant will actually help the nanoparticles stick to one another, creating a thin, uniform film of nanoparticles on a substrate. Generally nanoparticles described in this thesis are distributed drop-wise on to a glass substrate until a layer is thick enough to get a decent reading from the plot.

The X-ray diffractometer used for the work in this thesis is a Bruker AXS model D8 Focus. The x-ray radiation is Cu-Kα (λ=1.5406 Å). The detector is a 1D LynxEye Detector with a spatial resolution of 75 µm.

### 4.2 Transmission Electron Microscopy

#### 4.2.1 Basic Principles of TEM

This spectroscopy technique involves probing a material by the transmitting electrons, rather than light, through the sample [46]. Therefore, electromagnetic (EM) lenses must be used, rather than regular optical lenses. EM lenses work by
utilizing the Lorentz force; as magnetic field is changed, this will tune the focus on the lens and the resulting image.

The orientation of a TEM is similar to that of a transmission optical microscope, as shown in figure 4-4. Electrons are sent out of an electron gun at various accelerating voltages, depending on the make and model of the device. The electrons then pass through a series of lenses to fine-tune the beam before contact with the sample. The sample is sandwiched between two objective lenses. The first image is then created and projected onto a fluorescent screen.

![Schematic diagram of a transmission electron microscope (TEM)](image)

**Figure 4-4:** Schematic diagram of a transmission electron microscope (TEM) [48].

There are three different types of contrast associated with TEM: mass-thickness contrast, diffraction contrast and phase contrast. Mass-thickness contrast arises from sample thickness and specimen density [46]. Thus, a TEM image will appear darker in regions where the sample is thicker or denser than in other regions. Mass-thickness contrast issues commonly occur with large samples, such as
biological samples. Since the electrons used for imaging are both direct and diffracted electrons, *diffraction contrast* arises, as well [46]. This type of contrast comes from the stacking of atoms in a crystalline lattice. With a perfect crystalline lattice, all of the atoms will be aligned in the same place throughout the sample, and thus diffraction and contrast will become more pronounced. Likewise, defects in a crystalline lattice can reduce the amount of contrast that is inherent in a given sample, much like with XRD. This is the reason that it is impossible to achieve a clean HRTEM image of amorphous samples. Also, it is possible that a phase difference can exist between the direct and diffracted electrons after contact with the sample. This phase difference produces *phase contrast* [46]. Phase contrast gives rise to bright or dark field images. If enough tilt exists on the incident electron beam, a dark-field TEM image is produced, where the objects being viewed appear very light on a very dark background, opposed to the typical bright field image, where the opposite occurs. Only bright field TEM images are used throughout this thesis.

### 4.2.2 Sample Preparation for TEM

For transmission through a sample to happen, it must be transparent for electrons. This generally translates to a sample thickness of up to 500 nm for TEM or up to 100 nm for high resolution TEM. A charge-coupled device (CCD) camera is used to view the sample image on a fluorescent screen.

Since samples to be viewed using the TEM have a maximum observable thickness, this limits sample preparation techniques and types of samples that can be viewed using TEM. Standard TEM sample holders are made to hold samples that are 3 mm in diameter, which adds another sample preparation limitation. Bulk samples must be re-sized before viewing. This can be done a variety of ways.
including mechanical thinning, electrochemical thinning, ion milling, and focused ion beam [46].

All samples for this research were prepared on a 300 mesh formvar/carbon coated grid. Samples were prepared by first diluting the synthesized ferrofluid (1 drop of concentrated ferrofluid per 2mL of hexane) and then placing one drop of the dilute solution onto one TEM grid. The solvent is then evaporated, leaving a thin layer of nanoparticles on the grid. The samples were then mounted in the TEM and measurements were taken, as shown in figure 4-5.

![TEM Image](image.png)

**Figure 4-5:** Typical TEM image of nanoparticles (nickel ferrite) synthesized by thermal decomposition, accompanied by a histogram of particle size.

Particle size was measured using AnalySIS software with the *measure arbitrary distance* option. Average particle size was found by measuring many of the nanoparticles in the TEM’s computer system; error was determined by calculating the standard deviation from the average particle size.

The TEM used for this thesis is an FEI Morgagni 268 TEM at an accelerating voltage of 60 kV. The images were taken with an Olympus SIS MegaView III digital camera using. The operating magnification of the microscope is from 880x to
180,000x. High resolution TEM images for this thesis were taken at the University of South Florida’s Nanotechnology Research and Education Center by Dr. Yusuf Emirov using a Tecnai F20 TEM with an accelerating voltage of 200 kV. The operating magnification of the microscope is from 25x to 1,030,000x.

4.3 Magnetic Measurements

All magnetic measurements were taken using a Physical Property Measurement System (PPMS) by Quantum Design. The PPMS has a temperature range of 2-350K and can reach magnetic fields of up to ±7 Tesla using a liquid helium-cooled superconducting magnet. The PPMS has many different probes that can be used to make measurements. The probe that was used for the work in this thesis was the alternating current measurement system (ACMS) probe. The ACMS probe works based on Lenz’ Law, meaning that as a magnetic material is moved through the coil, a current is induced in the coil and a signal is measured.

4.3.1 Magnetization as a Function of Temperature

To characterize a sample, many measurements are necessary. The magnetization as a function of temperature \([M(T)]\) measurement is used to determine where magnetic transitions occur. There are two methods to recording \(M(T)\) measurements that were used for the research presented in this thesis: zero-field cooled (ZFC) and field-cooled warming (FCW).

In the ZFC portion of a plot, the sample is cooled down to below its magnetic transition temperature in the absence of an external magnetic field. Once the sample is at the base temperature, a small, constant external magnetic field, 100 Oe for the presented work, is applied to the sample and data points are taken as the sample is warmed. In the FCW portion of a plot, the sample is cooled back down to
below its magnetic transition temperature in the presence of the same, small external magnetic field. Once the sample reaches its base temperature, data points are taken as the sample is once again warmed.

In this thesis the ZFC and FCW curves provide information on the magnetic transition within the samples and also indicate size distribution of the nanoparticles. The ZFC curve provides information on the magnetic blocking temperature \( T_B \), which is similar to a Curie temperature \( T_C \). The \( T_B \) is proportional to the anisotropy constant \( K_u \) and magnetic volume \( V \) of the particle via

\[
T_B = K_u V / 25k_B ,
\]

where \( k_B \) is the Boltzmann constant \([14]\). The \( T_B \) is where the transition from the ferro- or ferrimagnetic to superparamagnetic states occurs while warming. This transition is indicated by a peak in the ZFC curve. The broadness of this peak serves as an indicator of the size distribution of the nanoparticles within various samples; the broader the peak, the larger the size distribution \([22]\). This is because as the size of the nanoparticles changes, the temperature where magnetic blocking occurs changes also. Larger nanoparticles tend to have higher blocking temperatures, and smaller nanoparticles tend to have lower blocking temperatures as seen in figure 4-6.

The temperature below which the ZFC and FCW curves begin to separate from each other is referred as to the irreversibility temperature \( T_{irr} \), which is often associated with the magnetic blocking of the largest particles. Figure 4-6 (B) shows a particle system where \( T_{irr} \) is well above \( T_B \) when compared with figure 4-6 (A). Systems such as this one often show a large particle size distribution \([27, 49-54]\). Above \( T_{irr} \), the system enters a fully superparamagnetic regime. Unless specified, the results presented and discussed in this section are for assemblies of spherical nanoparticles.

It can be seen in Figure 4-6 that both samples undergo a transition from the
Figure 4-6: ZFC and FCW magnetization vs. temperature [M(T)] curves of magnetite (Fe$_3$O$_4$) with two different sizes of (A) 6 nm and (B) 14 nm [14].

ferro- or ferrimagnetic (blocked) state to the superparamagnetic state with increasing temperature. The narrow shape of the ZFC MT curve observed for 6 nm Fe$_3$O$_4$ nanoparticles is consistent with the perspective of an assembly of weakly interacting single domain (SD) particles, whereas the broadening of the ZFC MT curve observed for 14 nm Fe$_3$O$_4$ nanoparticles points to the system with stronger dipolar inter-particle interactions [53].

4.3.2 Magnetization as a Function of Applied Magnetic Field

This measurement further probes the sample by measuring the magnetic moment as a function of applied magnetic field (MH). The magnetic moment of a sample is recorded as the external magnetic field is changed from positive to negative values. Since, in this thesis, only ferrites in the ferrimagnetic and superparamagnetic regimes are studied, these are the MH curves that will be
discussed. It is important to note that in the ferrimagnetic state \((T < T_B)\), the saturation magnetization \((M_S)\) and the coercivity \((H_C)\) increase as temperature decreases as seen in figure 4-7.

![Magnetization vs. Magnetic Field](image)

**Figure 4-7:** Example of magnetization vs. magnetic field \([M(H)]\) curves in the ferrimagnetic (red) and superparamagnetic (black) regions for nickel ferrite nanoparticles.

Goya *et al.* [27, 55] reported that with decreasing particle size from 150 nm to 4 nm, the \(H_C\) first decreased from 150 nm to 11.5 nm but increased sharply for the smallest particles \((D = 4\) nm). Dutta *et al.* [27] observed a slight increase in \(H_C\) as particle size was decreased from 12 nm to 6 nm and a sudden increase for 4 nm \(\text{Fe}_3\text{O}_4\) nanoparticles. In both cases, the strong increase of \(H_C\) for 4 nm \(\text{Fe}_3\text{O}_4\) nanoparticles is associated with the strong decrease of \(M_S\), both of which pointed to a strong surface spin disorder that is present in these systems.

Figure (4.7) shows the magnetic field dependence of magnetization \([M(H)]\) curves taken at 10 K and 300 K for 7 nm nickel ferrite \((\text{NiFe}_2\text{O}_4, \text{NFO})\) nanoparticles. The \(M(H)\) curves at 300 K do not show any hysteresis, whereas a clear hysteresis with a coercivity of \(H_C\) 138 Oe is observed at 10 K, which are characteristic of superparamagnetism and ferrimagnetism, respectively.
4.3.3 Sample Preparation for Magnetic Measurements

There are two ways to prepare nanoparticle samples for the PPMS. One method is to drop small amounts of concentrated ferrofluid into a gel cap and let the solvent evaporate. The other method is to drop concentrated ferrofluid onto a glass slide, let it dry, scrape the material off of the slide, and place the sample into a gel cap for measurement. Teflon tape fills the empty space within the gel cap to help keep the sample in place. The sample is then placed on the end of an ACMS probe and a measurement is set up.

To create a PNC sample, a similar method is utilized. Extra solvent is added to the PNC solution to make it less viscous and easier to work with. The material is then dropped on to a glass slide and left to dry. Once completely dry, the sample is placed in an oven and heated until the PNC is completely cured. Once the curing is finished, the sample is scraped off of the glass slide and placed in to a gel cap for measurement. Teflon tape, once again, fills the empty space within the gel cap and to help keep the sample in place and the prepared sample is placed on the end of an ACMS probe to make a measurement.
Chapter 5: Structure and Properties of Ferrite NPs and PNCs

This chapter will focus on structure and properties of ferrite nanoparticles and polymer nanocomposites made with them. The nanoparticles discussed are magnetite (Fe$_3$O$_4$) and cobalt ferrite (CFO) and they are housed in Rogers Polymer (RP) and polyvinylidene fluoride (PVDF).

5.1 Magnetite in Rogers Polymer (Fe$_3$O$_4$ in RP)

Due to well-studied magnetic characteristics of Fe$_3$O$_4$ and the low-loss nature of RP, a combination of these two materials was chosen as a starting point for PNC study. The synthesis procedure for the Fe$_3$O$_4$ nanoparticles is a thermal decomposition method[11], where 2 mmol of iron acetylacetonate [Fe(acac)$_3$] and 10-mL of oleylamine were added to 10-mL of benzyl ether. The solution was magnetically stirred under a continuous flow of argon at 110° C for 1 h, and then heated to reflux at 300° C for 2 h. The resultant black-colored material was left to cool to room temperature in an argon atmosphere. Then, 50 mL of ethanol was added to the solution and the precipitate was collected by centrifugation and washed with ethanol three times. The particles were then dissolved in hexane in the presence of oleic acid to stabilize the particles. Finally, the product was dried at room temperature and incorporated into RP following the procedure [11, 18, 44], previously discussed in chapter 3 and an 80 wt-% PNC was created.
5.1.1 Transmission Electron Microscopy (TEM)

The TEM image of this early film shows that the 8±1 nm Fe$_3$O$_4$ nanoparticles are evenly-spaced throughout the PNC film.

![TEM Image](image.png)

**Figure 5-1:** Transmission electron microscope (TEM) image of PNC consisting of magnetite (Fe$_3$O$_4$) in Rogers Polymer (RP) [11, 44].

In figure 5-1 we see some areas of uneven contrast due to uneven thicknesses across the film. Thickness contrast was previously discussed in chapter 4 [46]. The small, dark spots are the nanoparticles and the larger shaded areas are regions in the film where the polymer is not evenly coated on the TEM grid. This was the first attempt at viewing a nanoparticle-RP film using TEM and the methods were improved upon in subsequent samples.

5.1.2 Magnetometry Measurements

All of the standard magnetometry measurements were made using the ACMS option in the PPMS, previously described in chapter 4. Figure 5-2 shows the magnetization as a function of magnetic field [M(H)] at 300K for the 80 wt-% PNC and the pure Fe$_3$O$_4$ nanoparticles. From these curves, we see that there is a lack of coercivity, indicating that, in both cases, the nanoparticles appear to be in the superparamagnetic regime. The saturation magnetization (M$_s$) is significantly higher, 53 emu/g vs. 31 emu/g, for the plain nanoparticles opposed to the 80 wt-% PNC.
This is to be expected, as the magnetic volume in the 80 wt-% PNC is less than that of the pure Fe$_3$O$_4$ nanoparticles, and the dipolar interparticle interaction is weaker in the 80 wt-% PNC than in the pure Fe$_3$O$_4$ nanoparticles.

Figure 5-2: Magnetization vs. magnetic field (M(H)) loops taken at T=300K for plain Fe$_3$O$_4$ nanoparticles and the 80 wt-% PNC [11, 44].

Also note the smooth edge of the curve prior to saturation. This is due to thermal fluctuations allowing for more favorable flipping of magnetic moments of the Fe$_3$O$_4$ nanoparticles in the superparamagnetic state.

5.2 Cobalt Ferrite in Rogers Polymer (CFO in RP)

The next step in this project was to experiment with a different type nanoparticle in the same polymer matrix. Cobalt ferrite (CFO) was chosen as the candidate material due to similarities in crystalline structure and vastly different magnetic properties, such as blocking temperature (T$_B$) and coercivity (H$_C$)[18]. CFO also has inherently different microwave properties, which will be further discussed in chapter 6.

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The CFO nanoparticles were also made by thermal decomposition, however the procedure varied slightly from that of the Fe₃O₄ synthesis. In this procedure, we took 2 mmol of a mixture of cobalt (II) acetylacetonate [Co(acac)₂] and iron (III) acetylacetonate [Fe(acac)₃] in 1:2 ratio by mass [18, 36]. Then the mixture was added to 10 mmol of 1,2 hexadecanediol, 6 mmol of oleic acid, 6 mmol of oleylamine, and 20 mL benzyl ether. The mixture was heated to 200° C and maintained for 2 hours with constant stirring by magnetic stir bar and then refluxed at 300° C for 1 hour in the presence of Ar gas. The reaction mixture was allowed to cool to room temperature and ethanol was added to the cooled mixture. The black precipitate was separated by centrifugation. The final product of CFO nanoparticles was dispersed in hexane.

For this experiment, four samples were made: 30 wt-%, 50 wt-%, 80 wt-% and pure CFO nanoparticles (100 wt-%). These samples were made so that we could compare and probe the differences between various weight percentages using the same materials.

5.2.1 X-Ray Diffraction

As discussed in the previous chapter, XRD is used to probe the crystallinity of a sample. In our case, we also used it to compare the different weight percentages of PNC. Using XRD, we were able to see if creating a PNC out of CFO nanoparticles would, in any way, change their crystalline structure either from creating the PNC solution, or the subsequent drying and curing of the PNC. As seen from the XRD comparison plot in figure 5-3, the structure of CFO nanoparticles appears to remain intact.
Figure 5-3: X-ray diffraction (XRD) plot showing peaks in the same location and of comparable intensity for plain cobalt ferrite (CFO) nanoparticles and the 30 and 80 wt-% PNCs.

We see that peaks for the lowest and highest (30 and 80 wt-%) PNCs match each other and the pure CFO sample. The XRD plot shows noise because of the size of the nanoparticles. As grain size decreases to smaller and smaller values, the XRD readout can become noisy. The important part is that the peaks are in the same location, indicating an inverse spinel structure for all samples.

5.2.2 Transmission Electron Microscopy

TEM was used to confirm the size and shape of the CFO nanoparticles and the uniformity of each of the PNC films. TEM images were taken for each of the weight percentages and for the plain CFO nanoparticles, as seen in figure 5-4.

Figure 5-4: TEM images of (left to right) plain CFO nanoparticles, 30, 50, and 80 wt-% PNCs [18].
From the TEM images, we can see that the CFO nanoparticles are 10±1 nm in diameter and display no obvious indications of agglomeration over the various samples. Several regions of each sample were viewed, and well-separated particles were observed across all samples. It is clear to see that the inter-particle separation is greatest in the 30 wt-% PNC and least in the 80 wt-% PNC, with the 50 wt-% PNC falling in between the upper and lower bounds.

High resolution TEM (HRTEM) images were taken of the plain particles and the 50 wt-% PNC to more closely observe the synthesized samples, seen in figure 5-5.

![HRTEM images of plain CFO nanoparticles (left) and 50 wt-% PNC (right) showing amorphous regions where polymer is located](image)

Figure 5-5: HRTEM images of plain CFO nanoparticles (left) and 50 wt-% PNC (right) showing amorphous regions where polymer is located [18].

From the images of the plain CFO nanoparticles, it is clear to see that there is no agglomeration of nanoparticles. The right image shows a closer view of the 50 wt-% PNC, where we can see that there are clear boundaries between the nanoparticles and the polymer matrix. It is important to note that since the polymer is an amorphous material, it appears as regions of lower contrast when using the HRTEM [46].

### 5.2.3 Magnetometry Measurements

All magnetic measurements were made in a Quantum Design physical property measurement system (PPMS), as described in chapter 4. The standard magnetometry measurements were made, including temperature-dependent and external magnetic field-dependent magnetization \([M(T)\) and \(M(H)\), respectively].
These measurements, for all four samples are shown in figure 5-6. The M(T) measurement on the left in figure 5-6 was taken under the influence of a 100 Oe external magnetic field over a temperature range of 10-330K. The ZFC and FCW curves show a uniform blocking temperature of $T_B=298K$ for all samples, which shows that blocking is not altered by PNC loading or by any part of the PNC synthesis or curing processes. The uniform blocking temperature of the four samples also indicates that the surfactant coating on the nanoparticles is robust and remained preserved during the PNC formation.

Figure 5-6: Magnetometry measurements for CFO in RP samples. From left to right: M(T), M(H) at 10K, and M(H) at 300K measurements with inset showing close-up to show lack of $H_C$ in M(H) at 300K [18].

This observation is very important for tunable microwave applications, as problems with particle dispersion are known to affect the response and often yield results that are not reproducible from sample to sample. One advantage to using CFO nanoparticles near 10 nm in diameter as the filler is that their $T_B$ is so close to room temperature. Since this is the case, it is possible to access either the superparamagnetic or blocked state by heating or cooling the sample slightly, allowing for different commercial applications that require soft or hard magnetic properties of filler nanoparticles.

The M(H) measurements were conducted in external fields of up to ±50 kOe at temperatures of 10K (middle) and 300K (right). From the M(H) at 10K, we
observe a high $H_c$ of 19 kOe that is unchanging throughout the samples. The remnant ratio (ratio of remnant magnetization to saturation magnetization, $M_R/M_S$) is consistent for all samples at 10K also, as shown in table 1.

**Table 1:** Remnant magnetization, saturation magnetization and remnant ratio for each CFO in RP PNC, taken from the M(H) data at T=10K [18].

<table>
<thead>
<tr>
<th>Wt-% of CFO in RP</th>
<th>$M_R$ (emu/g)</th>
<th>$M_S$ (emu/g)</th>
<th>$M_R/M_S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>9</td>
<td>11</td>
<td>0.82</td>
</tr>
<tr>
<td>50</td>
<td>17</td>
<td>20</td>
<td>0.85</td>
</tr>
<tr>
<td>80</td>
<td>27</td>
<td>32</td>
<td>0.84</td>
</tr>
<tr>
<td>100</td>
<td>38</td>
<td>45</td>
<td>0.84</td>
</tr>
</tbody>
</table>

At 300K, $H_c$=0 Oe, as well as exhibiting an $M_S$, which are characteristic of superparamagnetism in nanoparticles. It is important to note that in all cases, the magnetization value increases with increasing CFO loading in the samples, which means that the magnetization of these PNCs can be tuned based on nanoparticle loading.

### 5.3 Magnetite in Polyvinylidene Fluoride ($\text{Fe}_3\text{O}_4$ in PVDF)

As a third step in this project, we decided to experiment with a different type of polymer and went back to $\text{Fe}_3\text{O}_4$ as the magnetic nanoparticle filler. Polyvinylidene fluoride (PVDF) was chosen because of its piezoelectric properties [3]. The dispersion of nanoparticles into this polymer matrix served more difficult than with the previous samples because PVDF is water-soluble, meaning that a new type of surface functionalization was needed on the nanoparticles. The $\text{Fe}_3\text{O}_4$ nanoparticles have been functionalized with Polyethylene glycol (PEG), an amphiphilic polymer.

$\text{Fe}_3\text{O}_4$ nanoparticles were synthesized in the same manner as in chapter 5.1 [11]. Surface functionalization was carried out by dissolving polyethylene glycol (M
= 3000), N-hydroxysuccinimide, N,N′-dicyclohexylcarbodiimide and dopamine hydrochloride in a mixture containing chloroform, dimethylformamide and anhydrous sodium carbonate. The solution was stirred at room temperature for 2 h before Fe₃O₄ nanoparticles were added, and the resulting solution was stirred overnight at room temperature in an argon atmosphere [56]. The surface functionalized Fe₃O₄ nanoparticles were precipitated by adding hexane and dried under argon. The resulting surface functionalized Fe₃O₄ nanoparticles were suspended in a solution containing dimethylformamide and PVDF to make 30 wt-%, 50 wt-%, and 80 wt-% PNCs.

5.3.1 Transmission Electron Microscopy

Figure 5-7 shows TEM images of the 50 wt-% PNC and of plain Fe₃O₄ nanoparticles (100 wt-%).

![TEM images](image)

**Figure 5-7:** TEM images of plain Fe₃O₄ nanoparticles (left) and the 50 wt-% PNC consisting of Fe₃O₄ in polyvinylidene fluoride (PVDF) (right).

Fe₃O₄ nanoparticles are 7±2 nm in diameter and display no obvious indications of agglomeration over multiple regions of each sample.

5.3.2 Magnetometry Measurements

M(T) and M(H) measurements were made for all four samples to compare the magnetic characteristics of each PNC. The measurements for all samples are seen below.
Figure 5-8: Magnetometry measurements for Fe$_3$O$_4$ in PVDF samples. From left to right: $M(T)$, $M(H)$ at 10K, and $M(H)$ at 300K measurements. Insets show close-ups to show $H_C\neq 0$ from $M(H)$ at 10K and $H_C=0$ from $M(H)$ at 300K.

The $M(T)$ measurements on the left in figure 5-8 were taken under the influence of a 100 Oe external magnetic field over a temperature range of 10-300K. The ZFC and FCW curves show a uniform blocking temperature of $T_B\approx 40$K for all samples, which shows that, as with previous samples, blocking is not altered by PNC loading or by any part of the PNC formation or curing processes.

The $M(H)$ measurements were conducted in external fields of up to $\pm 50$ kOe at temperatures of 10K (middle) and 300K (right). From the $M(H)$ at 10K, we observe a $H_C$ of 185 kOe that is constant throughout the samples. The remnant ratio (ratio of remnant magnetization to saturation magnetization, $M_R/M_S$) is also consistent for all samples at 10K also, as shown in table 2.

Table 2: Remnant magnetization, saturation magnetization and remnant ratio for each Fe$_3$O$_4$ in PVDF PNC, taken from the $M(H)$ data at $T=10$K.

<table>
<thead>
<tr>
<th>Wt-% of Fe$_3$O$_4$ in PVDF</th>
<th>$M_R$ (emu/g)</th>
<th>$M_S$ (emu/g)</th>
<th>$M_R/M_S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.53</td>
<td>1.60</td>
<td>0.33</td>
</tr>
<tr>
<td>50</td>
<td>1.30</td>
<td>4.20</td>
<td>0.31</td>
</tr>
<tr>
<td>80</td>
<td>1.86</td>
<td>6.12</td>
<td>0.30</td>
</tr>
<tr>
<td>100</td>
<td>2.34</td>
<td>7.12</td>
<td>0.33</td>
</tr>
</tbody>
</table>

At 300K, all samples appear to be superparamagnetic due to finite $M_S$ values and a lack of $H_C$. In all samples, the $M_S$ increases with increasing nanoparticle concentration, which means that the magnetization of these PNCs can also be tuned based on nanoparticle loading, which turns out to be very important with microwave
tunability measurements. This phenomenon has been observed with iron nanoparticles (~20nm) in poly(methylmethacrylate) (PMMA) [1].
Chapter 6: Microwave Properties of PNCs

6.1 Background and Theory on Microwaves and Radio Frequency (RF) Characterization

All tunability measurements were conducted in the Center for Wireless And Microwave Information Systems (WAMI) in the department of Electrical Engineering at the University of South Florida under the direction of Dr. Jing Wang and Dr. Tom Weller.

Dielectric permittivity and magnetic permeability are inherent in every material and are extremely important factors in the fabrication of microwave and RF devices. Generally, the necessary values for calculations are the relative permittivity and permeability. Relative dielectric permittivity is defined as

\[ \varepsilon_r = \frac{\varepsilon}{\varepsilon_0}, \]

where \( \varepsilon_0 = 8.85 \times 10^{-12} \text{ F/m} \) is the permittivity of free space, and \( \varepsilon \) is the absolute permittivity of a sample [19]. It is also important to note that \( \varepsilon_r = \varepsilon_{\text{eff}}' - i \varepsilon_{\text{eff}}'' \), where \( \varepsilon_{\text{eff}}' \) is the real part of the complex relative permittivity and \( \varepsilon_{\text{eff}}'' \) is the imaginary part.

Similarly, relative magnetic permeability is defined as

\[ \mu_r = \frac{\mu}{\mu_0}, \]

where \( \mu_0 = 4\pi \times 10^{-7} \text{ N/A}^2 \) is the permeability of free space and \( \mu \) is the absolute permeability [19]. It is also important to note that \( \mu_r = \mu_{\text{eff}}' - i \mu_{\text{eff}}'' \), where \( \mu_{\text{eff}}' \) is the real part of the complex relative permeability and \( \mu_{\text{eff}}'' \) is the imaginary part.
The loss tangent is another important figure of merit as it quantifies the amount of signal lost in a sample. The loss tangent is described by

\[ \tan \delta = \frac{\delta_r''}{\delta_r'} \tag{6.3} \]

where \( \delta_r' = \mu_r \varepsilon_r - \mu_r'' \varepsilon_r'' \) and \( \delta_r'' = \mu_r \varepsilon_r'' - \mu_r' \varepsilon_r' \). The loss tangent can also be expressed as the inverse of the quality factor (Q-factor) [57]. The Q-factor is defined as the ratio of energy transmitted through a sample to the energy dissipated in it and is another measure of how effective a sample can be.

The resonance frequency range dictates under which circumstances a device will operate. The resonance frequency is described by the following equation:

\[ f_r = \frac{v_p}{\lambda_g} = \frac{c}{\lambda_g \sqrt{\varepsilon_r \mu_r}}, \tag{6.4} \]

where \( v_p \) is phase velocity of the incident wave and \( \lambda_g \) is the guided wavelength, which is \( \lambda_g = \frac{2L}{n} \), where \( L \) is the length of an inner conducting material on a fabricated device, and \( n \) is the \( n^{th} \) frequency harmonic [58]. Therefore the resultant frequency of the resonator relies on the effective material properties of the substrate used.

Other microwave characteristics include the scattering parameters, or S-parameters. These are the reflection and transmission coefficients as signals are passed through a sample and are measured in decibels (dB) as a function of frequency [58]. These parameters are S11, S21, S12, and S22 for a two-port measurement. The reflection S-parameters are S11 and S22. S11 refers to the signal sent from port 1 and received at port 1; similarly, S22 refers to the signal sent from port 2 and received at port 2. The reflection S-parameters are commonly referred to as return loss. The transmission S-parameters are S21 and S12. S21 refers to the signal sent from port 1 and read at port 2; similarly, S12 refers to the signal sent from port 2 and read at port 1. The transmission S-parameters are commonly referred to as insertion loss. The S-parameters are the basis of all of the
other microwave characteristics. All other microwave characteristics are extrapolated from the S-parameters.

6.2 Microwave and RF Measurements

In the following samples, it is important to note that eddy currents are suppressed due to the monodispersion of superparamagnetic particles [59]. It has been shown that composites containing single domain filler materials (i.e. superparamagnetic particles) show higher values of permeability than their multi domain (MD) counterparts. MD samples, or samples with agglomerations of nanoparticles can lead to a lower value of permeability [60].

For this experiment, a two-port microstrip-based cavity resonator was designed to probe the magneto-dielectric properties in the RF and microwave regions for PNCs under the influence of an external DC magnetic field, provided by an electromagnet, transverse to the device. The magnetic field applied to the sample was measured using a DC magnetic flux meter. A schematic of the measurement set-up and a picture of the actual set-up are shown in figure 6-1.

![Schematic of test fixture set-up in electromagnet (left) and photo of set-up with cavity resonator (right)](image)

**Figure 6-1:** Schematic of test fixture set-up in electromagnet (left) and photo of set-up with cavity resonator (right) [11, 58].
Nonmagnetic SMA connectors and cables were used in the set-up to avoid any magnetic interference during measurements.

6.2.1 Magnetite in Rogers Polymer

For this sample, the microstrip-based cavity resonator was constructed by bonding two 635 µm-thick printed circuit board (PCB) laminates. The laminate material was Rogers RT/Duroid 6010LM, which offers a high dielectric constant, of 10.2 and boasts low losses of tanδ=0.0023 (as stated on Rogers Corporation fact sheet) [58]. The cavity resonator is comprised of the PNC, which is sandwiched in between the two sheets of PCB, with a copper ground plate on the bottom and a copper transmission line running along the top, as seen in figure 6-2 (below) and figure 6-1 (above).

![Figure 6-2: Schematic of cavity resonator [11, 44].](image)

The bottom laminate sheet was fabricated with a 435 µm cavity in which the PNC solution could be easily deposited and incorporated into the device.

The PNC solution was deposited into the cavity via volumetric syringe. After PNC deposition, the sample was left to dry overnight and the PNC was then cured at 90°C in an atmosphere of 686 torr for 4 hours. Once the PNC was cured in the cavity, the two PCBs were bound together using a thin layer of epoxy while applying a vacuum to avoid bubble formation in between the layers of this device.
All RF and microwave measurements were conducted at room temperature within the frequency range of 1-6 GHz using the thru-reflect-line calibration procedure [58]. Scattering parameters were measured in order to extract the microwave characteristics of the PNC. The Nicolson-Ross-Weir formulation was combined with a conformal mapping method to extract microwave properties [61-72]. All analysis of RF and microwave data was done using the electromagnetic simulation software, Ansoft HFSS v11.1, with errors of less than 3%.

The first set of data that will be presented in this chapter is of the 80 wt-% PNC consisting of Fe₃O₄ nanoparticles in RP. The unfilled RP exhibits a relative permittivity of 2.4 and a relative permeability of 1. In zero applied magnetic field, the relative permittivity of the PNC is close to 5.4; the nanoparticle inclusions are responsible for this jump.

As figure 6-3 shows, there is an increase in relative permittivity as both the external magnetic field and frequency are increased.

![Figure 6-3: Relative permittivity of the 80 wt-% Fe₃O₄ in RP PNC as a function of external magnetic field and frequency [11, 44].](image)
At 6 GHz, a maximum value for relative permittivity was found to be 5.96 when 
H=2.2 kOe. These figures demonstrate a maximum tunability of the relative 
permittivity of 5.5%.

Figure 6-4 shows the extracted values for relative permeability. The inclusion 
of Fe$_3$O$_4$ nanoparticles provides the PNC with a measurable value for permeability.

**Figure 6-4:** Relative permeability of the 80 wt-% Fe$_3$O$_4$ in RP PNC as a function of 
external magnetic field and frequency [11, 44].

The relative permeability was found to exhibit a maximum at H=0.9 kOe for all 
measured frequencies. This is a characteristic value associated with Fe$_3$O$_4$ 
nanoparticles. An overall maximum relative permeability of 1.92 was extracted from 
data at a frequency of 1 GHz. The lowest relative permeability of 1.4, also at 1 GHz, 
was found at H= 4 kOe. Using these values for maximum and minimum relative 
permeability, we determine that a maximum tunability of 37% is achieved with the 
application of an external magnetic field.

The loss tangent varies with frequency at H=0, as shown in figure 6-5.
Figure 6-5: Loss tangent of the 80 wt-% Fe$_3$O$_4$ in RP PNC as a function of external magnetic field with frequencies of 1-6 GHz [11]. The largest (0.14) and lowest (0.0011) losses are extracted at a frequency of 6 GHz for external magnetic fields of 2.6 kOe and 4.0 kOe, respectively, signifying a large external magnetic field dependence.

Figure 6-6: Transmission through the sample as a function of frequency over a variety of external magnetic fields for the 80 wt-% Fe$_3$O$_4$ in RP PNC showing changing resonance frequency [11, 44].
Figure 6-6 shows the measured transmission characteristic of the PNC in the cavity resonator as a function of frequency for a series of external magnetic fields ranging from zero to 3.95 kOe. From this plot, we see a clear pattern that as the external magnetic field is increased, the resonance frequency peak increases in value and becomes more pronounced. This change in resonance frequency is ascribed to variations in the relative permeability and relative permittivity of the PNC. Notably, the insertion loss decreases from -24.2 dB to -10.5 dB, with increase of external magnetic field, as evidenced by the magnitude of each resonance frequency peak. Figure 6-7 shows a comparison of quality factor and resonance frequency as a function of external magnetic field.

![Graph showing quality factor and resonance frequency](image)

**Figure 6-7:** Quality factor and resonance frequency as a function of external magnetic field for the 80 wt-% Fe₃O₄ in RP PNC [11, 44].

From this plot, we can see that there is an accessible resonance frequency range of 2.480 GHz to 2.537 GHz (a difference of 57 MHz) and that the Q-factor increases 5.4 times, with the application of an external magnetic field. It is important to note that the maximum Q-factor of 67 occurs at the maximum external magnetic field of 4 kOe.
6.2.2 Cobalt Ferrite in Rogers Polymer

For this set of samples, two-port microstrip test fixtures were designed for microwave characterization purposes [18]. The device, shown in figure 6-8 was designed to have a PNC layer with a transmission line (metallization layer) adhered to the top of it. The PNC and the metallization layer are sandwiched between a dielectric substrate and a layer of RP, with copper leads on top of the device and a copper ground plate on the bottom, creating a microstrip linear resonator (MLR).

![Diagram of microstrip linear resonator](image)

**Figure 6-8:** Schematic for microstrip linear resonator used for tunability measurements with the CFO in RP PNC [18].

This design was fabricated with liquid PNC solution deposition in mind. PNCs consisting of CFO and RP were drop-cast on to the dielectric substrate using a volumetric syringe.

Several of these structures were made to test three separate concentrations in order to study their magneto-dielectric response at various microwave frequencies under the influence of external magnetic field. The boards were dried overnight and cured in a vacuum oven at 110° C for 3 hours. A PNC film thickness of 100 µm was measured by profilometry.

Measured transmission characteristics of the PNCs in the MLR can be seen in figure 6-9 of the 80 wt-% PNC.
Figure 6-9: Transmission through the sample as a function of frequency over a variety of external magnetic fields for the 80 wt-% CFO in RP PNC [18].

This plot shows the microwave signal attenuation as a function of frequency for the 80 wt-% PNC under the influence of various external magnetic fields. As mentioned in equation 6-4, as either the permeability or the permittivity of a sample is altered, the resonance frequency will change. This translates to a variable peak in figure 6-9.

Figure 6-10 shows the quality factor (left) and resonance frequency (right) as a function of external DC magnetic field for the 30 wt-%, 50 wt-% and 80 wt-% PNCs.

Figure 6-10: Q-factor (left-axis) and resonance frequency (right-axis) as a function of external DC magnetic field for the 30 wt-% (left), 50 wt-% (middle) and 80 wt-% (right) PNCs [18].

From these plots, we can determine that each sample appears to follow a similar pattern with regard to increasing Q-factor and varying resonance frequency along
with increasing magnetic field. For the device with 80 wt-% loading, a strong deviation of 518 MHz (from 2.976 to 2.458 GHz) in the resonance frequency was observed, which implies that the product of $\mu$ and $\varepsilon$ experienced a significant variation under the application of an external magnetic field. Furthermore, the Q-factor was increased from 2.0 to 11.46 (5.6×). From these results, we can surmise that the incorporation of a high concentration of magnetic nanoparticles into a polymer matrix improves the tunability of the complex permittivity and complex permeability at microwave frequencies.

As compared to the 80 wt-% sample of CFO nanoparticles in RP, the samples with reduced loadings (50 wt-% and 30 wt-%) demonstrate subtle changes in their measured frequency responses under the influence of the externally applied magnetic field, as shown in figure 6-10. For the 50 wt-% and 30 wt-% PNCs, the resonance frequency deviated by just 5 MHz and 1.25 MHz, respectively. The corresponding Q-factors for the 50 wt-% and 30 wt-% PNCs were increased from 19.03 to 20.10 and 28.30 to 28.51, respectively. This data clearly shows that the tunability of the device is greatly dependent upon the concentration of nanoparticles in the PNC. However, as the incorporation of magnetic nanoparticles also introduces noticeably extra losses, a design strategy and trade off might be needed to achieve the best balance between the desired tunability and microwave performance of the devices.
Chapter 7: Conclusion and Future Works

7.1 Conclusion of Current Work

In conclusion, three separate polymer nanocomposites (PNCs) were synthesized and their structural, magnetic and microwave properties were studied systematically. Nanoparticle synthesis methods discussed in this thesis were chemical co-precipitation, microemulsion, and solvothermal synthesis methods with special emphasis on thermal decomposition that was exclusively used to make high-quality ferrite nanoparticles in this work. The thermal decomposition synthetic method involves the breakdown of reagents and formation of nanoparticles at elevated temperatures (~300°C). Magnetite (Fe$_3$O$_4$) and cobalt ferrite (CFO) nanoparticles were used as PNC fillers for their desirable magnetic and microwave properties. Polymers used in this work were Rogers Polymer (RP), a low-loss, high-temperature thermosetting resin, and polyvinylidene fluoride (PVDF), a piezoelectric polymer. PNCs were made using a solution mixing method, and cured in a vacuum oven. Characterization techniques for determining morphology of the nanoparticles and their resulting PNCs include x-ray diffraction, transmission electron microscopy and magnetometry. The three PNC systems that were discussed in this thesis are Fe$_3$O$_4$ in RP, CFO in RP and Fe$_3$O$_4$ in PVDF.

Magnetic measurement data revealed superparamagnetic behavior at room temperature for all PNCs. Important magnetic parameters, such as blocking temperature, coercivity and reduced remnant magnetization, do not vary with concentration. Tunable saturation magnetization, based on nanoparticle loading,
was observed across all PNCs, regardless of choice of polymer or nanoparticle, which indicates that this is an inherent property in all similar materials.

For the first tunability study, microwave properties of magneto-dielectric PNCs with 8-nm-diameter \( \text{Fe}_3\text{O}_4 \) nanoparticles have been extracted in the frequency range between 1–6 GHz. The relative permeability and permittivity of the nanocomposite material were extracted through the implementation of a conformal mapping method. Tunability of 5.5% in the permittivity, 37% in the permeability, and a loss tangent reduction of more than 100x, were observed in the presence of an external magnetic field of less than 4.5 kOe. These properties make this material very useful in the design of tunable RF components such as flexible electronics, attenuators, and antennas. In addition, its magneto-dielectric properties are useful for miniaturization and enhancing of the bandwidth properties of microwave devices. A multilayer microstrip resonant structure was implemented to demonstrate the potential of this nanocomposite material for tunable and low-loss microwave device applications. The observed variation in the resonance frequency, insertion loss, and quality factor of the fabricated prototype device with embedded PNCs clearly indicate a strong dependence on the external magnetic field.

For the second tunability study, we have successfully synthesized three different concentrations of 10±1 nm CFO in RP with uniform particle dispersion throughout the polymer matrix. A microstrip linear resonator (MLR) was designed to incorporate synthesized PNCs. This MLR was used to conduct a series of S-parameter measurements, which provided microwave and radio frequency characteristics for all PNCs under the influence of an external magnetic field. For the device with 80 wt% loading, a measured frequency tunability of 518 MHz, and marked enhancement of the quality factor from 2 to 11.46 (5.6-fold improvement) were achieved with an externally applied magnetic field of less than 4.5 kOe. The observed variations in the resonance frequency, insertion loss and quality factor of
the fabricated device clearly indicate the high sensitivity of the device to magnetic bias fields. The 50 wt-% and 30 wt-% PNCs displayed much smaller changes when compared to the 80 wt-% PNC.

Overall, the research results of the present thesis demonstrate the possibility of incorporating superparamagnetic nanoparticles into a polymer matrix to make functional nanocomposite materials for high-performance RF and microwave device applications.

7.2 Future Works

For future work, we would like to conduct a full microwave study on the Fe$_3$O$_4$ in PVDF PNC and also extend that work to include other types of ferrite materials, such as cobalt, nickel and manganese ferrites to probe multiferroic characteristics (using PVDF).

Another area of interest is the study of nanoparticle-filled carbon nanotubes (CNTs), which we have started brief work on. CNTs have stirred interest in many areas of current research because of their unique electrical properties and potential use in the biomedical field [73]. Cobalt ferrite-filled CNT synthesis is described in the schematic in figure 7-1. CFO-filled CNTs were made by a template-assisted chemical vapor deposition method, followed by a magnetically assisted capillary action that draws ferrofluid into the CNTs.
Figure 7-1: From left to right: Alumina template with pores, alumina template with carbon nanotubes lining the inner walls, permanent magnet draws ferrofluid into pores, alumina template with CFO-filled CNTs, and free-standing CFO-filled CNTs.

In early works, TEM images showed that 7± 1 nm CFO nanoparticles were successfully synthesized and multi-walled CNTs were partially filled, as shown in figure 7-2.

Figure 7-2: TEM images of CNTs (a), CFO nanoparticles (b), fully-filled CNTs (c), and partially-filled CNTs (d).

These high-aspect ratio magnetic nanostructures appear to have a tunable anisotropy in addition to enhanced magnetic interactions amongst the CNT-encapsulated magnetic nanoparticles. Enhanced magnetic interactions, seen in figure 7-3, include higher saturation magnetization and higher blocking temperature.
Figure 7-3: \(M(T)\) (left) and \(M(T)\) at 300K (right) measurements for CFO nanoparticles and CFO-filled CNTs. These properties are desirable for microwave devices and could possibly be extended to biosensing applications.


Appendices

Appendix I: Publications


Appendix II: Conference Presentations


**Appendix III: Patents**